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(57) Abstract A polymeric composite structure having a configuration of a bathtub and a process of manufacturing the structure is disclosed. The polymeric composite structure includes an acrylic shell (12) and a plastic molded backing layer (14) which is bonded to a non-finish side (21) of the acrylic shell. A fiber reinforced resin layer, preferably fiberglass, is adhered to the non-finish side of the acrylic shell. A weight bearing reinforcing structure (16), such as chip-board, is adhered to the non-finish side of the shell (21) and to the fiber reinforced layer embedded within the molded polymeric backing layer. The molded polymeric backing layer (14) is made from a cross-linked thermosetting polymer, preferably a polyester blend, which does not contain isocyanate. The backing is bonded to the non-finish side of the shell and surrounds the fiber reinforcing and weight bearing reinforcing structures (16). The fiber reinforcing layer is bonded to the shell by a silane based coupler. The backing layer also includes a curing promoter, a peroxide cross-linking promoter and a filler such as calcium carbonate, sand or other fillers. The composite structure is manufactured by a process which includes preforming an acrylic shell, reinforcing a non-finish side of the acrylic shell with a resinous mixture of reinforcing fibers by spray-up and roll-out techniques and arranging the reinforced shell in a mold with a non-finish side covering a reinforcing structure placed below the floor of the shell. An uncured mixture of the thermosetting polymeric backing and promoter is injected into the mold coating the non-finished side of the shell and covering reinforcing fibers and chip-board structure. The thermosetting backing material is cured sufficiently to permit demolding of the composite structure without damage. The shell is preferably primed with a silane based coupler prior to the reinforcing step. In an alternative manufacturing process, the spray-up reinforcing step is replaced by the placement of a fibrous mat within the mold, surrounding the non-finish side of the shell. The fibrous material may include a fiberglass woven or a mat material or it may include a preformed fibrous structure.

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POLYESTER BACKED ACRYLIC COMPOSITE MOLDED STRUCTURE

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BACKGROUND OF THE INVENTION

10 1. Field of the Invention

This invention relates to a polyester backed acrylic composite molded structure. More particularly, it relates to a composite structure having a polyester polymeric backing material applied during a molding process to an acrylic shell for manufacturing of lightweight durable articles such as sanitary fixtures including bathtubs, sinks, shower receptors, lavatories and the like which are a lightweight, and resist damage and delamination when subjected to impact, the weight of the user and thermal shock.

2. Background of the Related Art

25 In the development of bathroom and kitchen fixtures, as well as bathtubs, whirlpool tubs and other composite articles, the traditional porcelain-cast iron fixtures have gradually been replaced by lighter and more resilient composite structures. One of the difficulties 30 with the porcelain-cast iron and enameled fixtures has been their susceptibility impact damage and extreme weight which causes great difficulties in moving and installing large fixtures such as sinks, bathtubs and whirlpool tubs. The porcelain-cast iron and enameled fixtures did have the 35 advantage of having a very solid feel and a high weight bearing capability.

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1 Initial attempts by the industry to replace these
porcelain-cast iron fixtures proved difficult. The early
composite structures had a plastic, hollow feel and would
deform, crack, chip or delaminate when subjected to
5 impact, thermal shock, or the weight of the typical
bather. Also, these composite structures would often
delaminate, crack, craze or chip when subjected to impact
from the outside of the structure during manufacturing,
transportation and installation of the fixture.

10 A successful solution to these problems is
disclosed in U.S. Patent No. 4,664,982 to Genovese et al.,
and in U.S. Patent Application Serial No. 07/400,289 to
15 Kuszaj et al., the disclosure of both of these documents
are incorporated by reference herein. Both disclose
composite enamelled steel or stainless steel fixtures
which have the look and feel of the earlier porcelain-cast
iron fixtures. The structures are light, have high
20 structural strength, and resist delamination, chipping and
denting due to impact or thermal shock. The composite
structures are formed from a steel or stainless steel
which may be enamelled on one or both of its faces. The
excellent physical and mechanical properties are imparted
25 to these shells as a result of the chemical bonding of a
plastic layer to a non-finish side of the shell. The
preferred plastic layer is an isocyanate-modified
thermosetting unsaturated polyester or polyether foam
which is introduced into a mold containing the shell by
Reaction Injection Molding (RIM), or by reinforced
30 reaction injection molding ("RRIM") processing. The
foamed plastic is chemically bonded to the shell by the
action of silane, a coupling agent which creates chemical
linkages between the metallic groups or the SiOH groups in
the enamel and the reinforced foamed plastic to form the
35 laminate. These composite structures possess excellent
physical and mechanical properties as a result of the
chemical bonding of the reinforced foamed polymeric layer
to the enamel steel or stainless steel shell. These

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1 disclosures do not relate, however, to the manufacture of
a composite structure in which an acrylic layer is bonded
to a polymeric or plastic molded structure. Additionally,
these reaction molding processes are carried out under
5 high pressures and require a large and expensive hydraulic
press to keep the mold closed and prevent the escape of
the reacting polymeric foam during the molding process.
Although these molding procedures result in a very fast
10 cure time, the equipment required, such as the hydraulic
mold press is expensive, requiring a high capital
investment.

Another solution to these problems was the use of a
15 polymeric, cosmetic surface layer bonded directly to a
foamed plastic substrate, described as a cross-linked
isocyanate-modified thermosetting unsaturated polyester or
polyether resin layer to provide a high impact strength,
delamination-resistant structure. These structures and
their process of manufacture are disclosed in U.S. Patent
20 Nos. 4,844,944 and 4,844,955 both to Graefe et al., the
disclosure of which is incorporated by reference herein.
Methylmethacrylate and commercially available adhesive
Thixon 416, manufactured by Whittaker Corp., West
Alexandria, Ohio, which contains a blend of 65% solvents,
25 35% solids including polyurethane phenolic and epoxy
resins, was used as a primer to cross-link and chemically
bond the polymeric cosmetic layer to the isocyanate groups
in the foamed plastic while plastic is cured. The
isocyanate was provided in the foamed plastic to provide a
30 very fast cure of the plastic layer during RIM, or RRIM
molding. These reaction molding processes are carried
out under high pressures and require a large and expensive
hydraulic press to keep the mold closed and prevent the
escape of the reacting polymeric foam during the molding
35 process. Although these molding procedures result in a
very fast cure time, the equipment required, such as the
hydraulic mold press is expensive, requiring a high
capital investment.

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1 Accordingly, a feature of the present invention is
to provide a polyester backed acrylic composite molded
structure which has a solid feel and sound of the
5 porcelain-coated cast iron and enameled fixtures without
the weight and delamination problems associated with such
structures.

Another feature of the present invention to provide
a polyester backed acrylic composite molded structure
10 which can be molded under low pressures without the need
for expensive hydraulic mold press which is needed for RIM
or RRIM molding.

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SUMMARY OF THE INVENTION

These and other features are achieved by the present invention which provides a polymeric composite structure, preferably formed in the configuration of a bathtub and a method manufacturing such composite structure. The polymeric composite structure includes a polymeric shell layer, preferably made from a thermoformable acrylic polymer of polymethylmethacrylate having a finish-side and a non-finish side. A fiber reinforced resin layer which may include a layer of fibers such as fiberglass, carbon, ceramic, boron, graphite, woolastonite, aromatic polyamide and mixtures of these fibers adhered to the non-finish side of the acrylic shell. Preferably such layers are made of chopped fiberglass in a resinous backing. A weight bearing reinforcing structure is adhered to the non-finish side of the shell and to the fiber reinforced resin layer. This weight bearing reinforcing structure can include wood, such as chip-board, particle-board, plywood and wooden planks or it may include a polymeric composite or inorganic weight bearing structures. Preferably, the weight bearing structure is a rectangular wooden structure made from chip-board placed below the floor portion of the bathtub. Additionally, a plurality of reinforcing wooden planks are placed below the deck portion of the shell of the tub.

Preferably, the non-finish side of the shell is bonded to the fiber reinforcing layer by a silane based coupler which is made from a silane based primer and a methylmethacrylate and solvent blend. The methylmethacrylate and solvent blend preferably includes methylene chloride, styrene and water, while the silane based primer composition suitably includes 3[2(vinyl benzylamino)ethylamino] propyltrimethoxy silane dissolved in a solution of toluene, butanol, 2-butoxy ethanol and ethyl alcohol.

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The polymeric composite also includes a molded, cross-linked thermosetting polymeric backing layer which surrounds the fiber reinforcing resin layer and the weight bearing reinforcing structure. The cross-linked thermosetting polymeric layer is bonded to the non-finish side of the polymeric shell and includes at least one of the following components: polyester, epoxy, acrylic, or vinyl esters, alone or blended in combination, but does not contain isocyanate. Preferably, this cross-linked thermosetting backing, prior to curing includes a rigid unsaturated polyester resin, flexible unsaturated polyester resin, a curing promoter, a peroxide cross-linking promoter and a filler in a ratio from about 2:1 resin to filler to about a 1:30 resin to filler. The filler may include calcium carbonate, aluminum trihydrate, glass spheres, sand, ceramic, mica, talc, silica, and mixtures containing one or more of these fillers.

20

The polymeric composite structure, preferably formed in the shape of the bathtub, is manufactured by a process of the present invention. The manufacturing process includes forming a polymeric shell, preferably a thermoformable acrylic shell of polymethylmethacrylate, to a suitable shape such as the configuration of a bathtub. The non-finish side of the polymeric shell is preferably primed with the above-described silane based coupler. The primed (or unprimed) polymeric shell is then reinforced on its non-finish side with a resinous mixture of reinforcing fibers by suitable spray-up and roll down, or by other suitable techniques. After the reinforced shell has sufficiently cured, the shell is arranged in a mold with the non-finish side covering a weight bearing reinforcing structure, such as chip-board, placed below the weight bearing portion of the shell, for instance, the floor of the tub. Other reinforcing structures such as wooden boards may be placed below the deck of the shell. An uncured mixture of unsaturated thermosetting polymeric

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1 backing material and cross-linking promoter, as described
above, is injected into the mold at a sufficient pressure
to force the backing material to coat the non-finish side
of the shell and cover the fiber reinforcing material and
5 the weight bearing reinforcing structures. The molded
thermosetting polymeric backing material is cured at
suitable temperatures and for a sufficient time to allow
hardening and cross-linking of the thermosetting material
and bonding of the fiber reinforcing layer structural
10 reinforcing non-finish side of the shell. After
sufficient curing, the composite structure is removed from
the mold for trimming.

In an alternative embodiment of this manufacturing
15 process, the polymeric shell, preferably primed (or
unprimed) is arranged in the molding cavity with the non-
finish side covering a fiberous reinforcement, such as a
fiberglass or other fiberous mat. An additional
fiberglass mat may be, preferably, placed between the
20 weight bearing reinforcing structure, such as the chip-
board, and the floor of the bathtub. The thermosetting
polymeric material is injected into the mold, coating the
non-finish side of the shell and embedding the fiberous
mat and the weight bearing board to bond these reinforcing
25 and weight bearing materials to the non-finish side of the
shell. It is also contemplated that the fiberous
reinforcing material such as fiberglass mat may be
inserted as a preformed fiberous structure made by a
thermoforming process, or the spray-up of fiberglass and
30 resin onto a suitably shaped screen.

For better understanding of the present invention,
references made to the following description, taken in
conjunction with the figures, the scope of which is
35 pointed out in the appended claims.

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BRIEF DESCRIPTION OF THE DRAWINGS

5 Figure 1 is a schematic partial perspective cross-sectional view illustrating the preferred polyester backed acrylic composite bathtub of the present invention.

Figure 2 is a schematic flow chart illustrating the low pressure resin transfer molding apparatus used to carry out the molding process of the present invention.

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Figure 3 is a top perspective view of the preferred molding receptacle in accordance with the present invention.

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Figure 4 is a perspective view of the mold according to the present invention shown in the open position, illustrating the molding receptacle, shell support and mold closing means of the present invention.

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Figure 5A shows the non-finish side of the acrylic shell of the present invention; and

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Figure 5B shows the non-finish side of the acrylic shell of the present invention after the application of fiberglass spray-up reinforcement.

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Figure 6 shows the freshly demolded polyester backed acrylic composite bathtub of the present invention positioned on a trimming table with a horizontally oriented circular saw for trimming excess polyester backing produced during the molding process, shown with blind bolts in place.

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Figures 7A, 7B and 7C are orthogonal views of the trimmed polyester backed acrylic composite bathtub of the present invention, shown without the blind bolts in place.

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DETAILED DESCRIPTION OF THE INVENTION

The polyester backed acrylic composite molded structure according to the present invention, preferably 5 molded in the configuration of a bathtub 10 is illustrated in Figure 1. Bathtub 10 includes a polymeric shell, preferably a thermoformable shell, most preferably an acrylic shell 12 having a polished finish side 20 which is normally exposed to the user. The shell 12 also includes 10 a non-finish side 21 which is bonded to molded thermosetting polymeric backing which does not contain isocyanate, preferably a blended polyester backing material 14. Additionally a fiberglass, graphite fiber, carbon fiber, boron fiber, ceramic fiber, woolastonite 15 fiber, aromatic polyamide fiber or similar reinforcing material (not shown) is preferably attached by spray-up prior to molding. Alternatively, the fiber reinforcing material is molded to the acrylic shell 12 by the polyester backing material 14 during the molding process. 20 A floor reinforcing means 16 preferably made of chip-board, particle-board or plywood is molded into the polyester backing 14 below the acrylic shell 12 under the floor of the bathtub 10. Preferably, deck supporting means 18, such as wooden boards are molded under the deck 25 area of the acrylic shell 12 within the polyester backing 14. In an especially preferred embodiment blind bolts 22 are placed, after the molding process has been completed, through a portion of the molded polyester backing material 14 and into the floor reinforcing means 16. Feet 24 are 30 attached to the blind bolts 22 for supporting the weight of the tub, user and water during bathing.

A schematic flow chart illustrating the preferred low pressure resin transfer molding (LPRTM) apparatus 25 35 suitable for carrying out the molding process of the present invention is shown in Figure 2. The molding apparatus 25 includes a mixer 26, such as a 110 gallon capacity NAUTA mixer manufactured by Daymixing Corp.,

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1 cincinnati, Ohio. The uncured, mixed polyester and filler
backing material is transferred from mixer 26 to a
pressure pot liner 28 which suitably fits within a
pressure pot 29, Model No. QM 5744 both of which are
5 manufactured by Devilbiss Corp., Toledo, Ohio. After the
addition of cross-linking promoter, the pressure pot 29 is
closed and compressed air 30 is pumped into the pressure
pot 29. Once pressure pot 29 is sufficiently charged,
throttle valve 32 is opened allowing the compressed air to
10 force the uncured polyester and filler mixture through
polymer delivery hose 34 and into the mold 36. Preferably
polymer delivery hose 34 is a flexible PVC hose having a
one (1") inch diameter which is disposed of and replaced
following the molding process. Mold 36 preferably
15 includes a molding receptacle 38, shown in Figure 3 made
from cast aluminum having a cavity for receiving the
acrylic shell 12, leaving a molding space between the non-
finish side 21 of acrylic shell 12 and an interior face 44
of the molding receptacle 38.

20

As illustrated in Figure 3, molding receptacle 38
is preferably made from a good heat dissipating material,
such as cast aluminum and has a relatively smooth interior
face 44 for forming the shape of the polyester backing 14.
25 Preferably, molding receptacle 38 also includes a water
jacket 45 or other temperature regulating means for
maintaining the mold 36 at a desired temperature (see
Figure 4). The uncured polyester backing and filler
mixture is introduced into the molding receptacle from
30 polymer delivery hose 34 into a molding aperture 46 which
is located approximately in the geometric center of a
portion of the molding receptacle 38 for molding the tub
floor. As shown in Figure 3, the interior face 44 of the
molding receptacle 38 includes a rectangular indentation
35 48 of suitable dimension to retain a tub floor
reinforcement 16, preferably a rectangular piece of chip-
board, or alternatively particle-board, plywood, wooden
plank, fiberboard or a composite, plastic, fiberglass or

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1 other suitable weight bearing structural reinforcing
material. The molding receptacle may suitably also
include positioners or slots (not shown) for retaining
deck supports 18, which preferably include wooden
5 reinforcing 1" by 1" boards illustrated in Figure 1.

Due to the low pressure molding process utilized in
the present invention, mold seals are not required, and in
fact may impede the flow of the uncured polyester resin
10 and filler mix into the cavity formed between the non-
finish side 21 of the acrylic shell 12 and the interior
face 40 of the molding receptacle 38. Due to the absence
of mold seals, there is some spillover of polyester
15 backing material 14 and adherence of the hardened backing
material to portions of the molding receptacle 38 due to
the molding and curing process. Accordingly, hydraulic
lifters are not ordinarily utilized. Rather, after the
polyester backing 14 is sufficiently cured the molded tub
is loosened or cut from the molding receptacle 38 and
20 removed by hand.

The mold 36 also includes a shell support and mold
closing means 40 which maintains the shape of the thin
acrylic shell 12 during the molding process, and holds the
25 acrylic shell in proper orientation within the molding
receptacle 38. The mold may be kept closed by any
suitable means, however, due to the low molding and curing
pressures, an expensive hydraulic mold press which is
required in RIM and RRIM molding, although useful, is not
30 required. Rather four C clamps 42, rated at 500 lbs.
each, are entirely satisfactory for keeping mold 36 closed
during the molding and curing process.

The mold 36 as viewed in the open position is
35 illustrated in greater detail in Figure 4, showing the
molding receptacle 38, and shell support and mold closing
means 40 suitably held above the molding receptacle by a
mold opening and lifting means, such as a chain hoist 50.

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- 1 As well known by those skilled in the art other mold opening and closing means such as a pivoting or levered systems, electro-mechanical or hydraulic mold clamps may be suitably utilized to carry out the molding process of
- 5 the present invention instead of the chain hoist 50 and clamps 42.

The shell support and mold closing means 40 shown in Fig. 4 is typically made of a cast aluminum core 52 which is coated with a urethane skin 54 which matches the shape and supports the finish side 20 of the acrylic shell 12, without scratching or otherwise damaging the polished finish. Teflon strips 56, or other non-abrasive materials are included around the periphery of the urethane skin 52 for contacting and urging a deck portion of the shell 12 towards the molding receptacle 38 during the molding process without causing damage to the finish side 22 of deck portion of shell 12. A detailed description of other suitable molding apparatus which may be adapted for use with the present invention is described and commonly assigned co-pending U.S. Patent Application Serial No. 07/467,384 filed January 19, 1990 the disclosure of which is incorporated by reference herein.

25 In accordance with the process of the present invention acrylic shell 12 is formed from a cell cast acrylic sheet preferably made from polymethylmethacrylate which has a highly polished finish side and a non-finish side. The shell preferably has a thickness of

30 approximately 3.2 millimeters. The acrylic sheet may be made from other materials such as those described in United States Patent Nos. 4,844,955 and 4,844,944 the disclosure of which is incorporated by reference herein. The acrylic sheet is thermoformed using well known vacuum

35 thermoforming apparatus into the desired shape of the acrylic shell 12 which is illustrated in Figure 5A.

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1 The thermoformed acrylic shell 12 is preferably
treated on its non-finish side 21 with a bonding primer
composition. One suitable primer composition includes a
silane based primer AP-134, manufactured by Lord Corp. in
5 Erie, Pennsylvania. It contains a silane compound at a
10% concentration in a solvent of 75% toluene, 5% butanol,
5% 2-butoxy ethanol and 5% ethyl alcohol. A suitable
silane compound is 3[2(vinyl benzylamino)ethylamino]propyltrimethoxy silane at a preferred 10% concentration,
10 although the concentration of this silane compound may
range from about 1% to about 20%, preferably from about 5%
to about 15%. The silane primer AP-134 is most preferably
mixed at a 1% concentration by weight with 1% water, 9.8%
styrene, 29.4% methylene chloride and 58.8%
15 methylmethacrylate. The concentration of these components
may range from about 0.1% to 10%, preferably from about
0.5% to about 2% silane primer such as AP-134; from about
0.1% to about 10%, preferably from about 0.5% to about
2.0% water; from about 0.1% to about 98%, preferably from
20 about 5% to about 15%, styrene; from about 2.5% to about
98%, preferably from about 25% to about 35% methylene
chloride; and from about 98% to about 5%, preferably from
about 70% to about 40% methylmethacrylate. This primer
solution promotes cross-linking and improves bonding
25 between the polyester reinforced backing and the non-
finish side 21 of the acrylic shell. Other compositions
useful as bonding primer solutions are described in the
above-referenced U.S. Patent Nos. 4,844,955 and 4,844,944
to Graefe et al. The purpose of the primer is improve
30 bonding to the acrylic shell 12 allowing for faster
demolding times. However, if the demolding times are
increased, or if sufficient bonding occurs during the
spray up reinforcing step, the bonding primer is not
required.

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 The thermoformed and preferably primed acrylic
shell is reinforced with a resinous mixture of fiberous
material, including chopped fiberglass, ceramic fibers,

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1 boron fibers, graphite or carbon fibers, woolastonite
fibers, or aromatic polyamide fibers. Preferably, the
reinforcing materials include a sprayed on and rolled out
mixture of chopped fiberglass from about 10% to about 40%,
5 preferably from about 15% to about 35%, and most
preferably about 30% by weight; and polyester resin from
about 60% to about 90%, preferably from about 85% to about
75%, and most preferably about 70% by weight. The sprayed
10 on fiberglass is typically designated as fiberglass
reinforced plastic (FRP) or glass reinforced plastic
(GRP). The polyester resin preferably includes a mixture
of a rigid unsaturated polyester resin and styrene
monomer designated 31-439 by the Reichold Corp.; and may
also include a flexible unsaturated resin designated 97-
15 088 by Reichold Corp. and a styrene monomer. The
polyester resin is combined with a curing or cross-linking
promoter containing from about 0.01% to about 1%,
preferably from about 0.05% to about 0.5%, most preferably
about 0.2% cobalt naphthanate; and from about 0.1% to
20 about 5%, preferably from about 0.5 to about 3%, most
preferably about 1% methyl ethyl ketone peroxide,
percentages based on weight of resin only. The resin and
chopped fiberglass mixture is typically applied by
suitable spray equipment such as Venus Model HI SSCW 2100
25 manufactured by Venus-Gusmer Corp., Kent, Washington.
After curing for approximately one hour, the reinforced
acrylic shell 58 illustrated in Figure 5B is placed in the
molding receptacle 38 with reinforcing weight bearing
structures 16 and 18 placed below the tub floor and deck
30 regions, respectively.

In an alternative embodiment, the acrylic shell 12,
preferably primed as described above, is reinforced with a
matted or woven fibrous reinforcing material, as
35 described above, preferably a 1 & 1/2 ounce (per square
foot) fiberglass mat. The fibrous reinforcing material
is placed inside the molding receptor, preferably below
the weight bearing floor supporting board 16, and another

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1 fiber reinforcing mat is placed above the reinforcing board 16 and below the floor of shell 12. The fiberglass or similar mat of fiberous reinforcing material is adhered to the acrylic shell 12 during the molding step. A
5 further alternative is that the fiberous reinforcing material is preformed prior to the molding step and placed as a single unit inside the molding receptacle 38 prior to the placement of the reinforcing board 16 and acrylic shell 12 within the molding receptacle 38. Preforming of
10 the fiberglass reinforcing material may be obtained using thermoformable fiberglass and plastic composite or similar fibrorous composite which is shaped using thermoforming techniques which are well known to those skilled in the art. Alternatively, preforming may be accomplished by
15 spray-up of a resinous mixture of chopped fiberglass or other fibers onto a shaped mesh or screen by known techniques.

After the acrylic shell has been suitably arranged
20 within the molding receptor, the mold 36 is closed by placing the urethane coated surface 54 and TEFILON strips 56 of the shell support and mold closing means 40 in suitable contact with the finish-side 21 of the acrylic shell 12. The mold is suitably clamped to provide
25 sufficient venting by four heavy duty C clamps 42 to secure the shell support and mold closing means to the molding receptacle 38. After the mold has been secured and properly vented, the temperature of the mold is stabilized between 100° and 120° F using a water jacket 45
30 in the molding receptacle 38.

The low pressure resin transfer molding (LPRTM) process suitable for the present invention is described below, however, other low pressure injection, gravity
35 casting or displacement molding processes may also be suitably adapted for use in the present invention. The preferred resin, filler and catalyst formulation is described below.

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Typically, approximately 100 lbs. of material is mixed in mixer 26, thus the percentages are based on weight. The most preferred polyester resin and filler 5 formulation includes rigid unsaturated polyester resin and styrene monomer, sold under the name Reichhold 31-439, 35.20%; flexible unsaturated polyester resin and styrene monomer sold under the name Reichhold 97-088, 11.90%; styrene monomer, 2.48%; calcium carbonate (filler), sold 10 under the name Vicron 15-15, 49.6%; dimethylparatoluidene (DMPT) (activator/promoter), 0.6%; benzoyl peroxide, sold under the name Cadox 40 E (40% benzyl peroxide solution), 0.76%. Suitable ranges of this preferred combination of materials include from about 0% to about 98%, preferably 15 from about 25% to about 45% Reichnold 31-439; from about 98% to about 0%, preferably from about 20% to about 5% Reichnold 97-088; from about 0% to about 40%, preferably from about 1% to about 10% styrene; from about 0% to about 75%, preferably from about 40% to about 60% Vicron 15-15; 20 from about 0.05% to about 5%, preferably from about 0.2% to about 1% DMPT; and from about 0.05% to about 5%, preferably from about 0.2% to about 2% Cadox 40E.

25

Depending on the type of filler used, the ratio of resin to filler may range from no filler at all, or it may be as high as 1:30, depending upon the filler particle size. Preferably the ratio of resin to filler may be from about 2:1 to about 1:3. Other fillers may be added in addition to or instead of calcium carbonate, including 30 aluminum trihydrate, glass spheres, sand, ceramic, mica, talc, silica and other suitable filling materials. Various other fillers are described in U.S. Patent Nos. 4,844,955 and 4,844,944 to Graefe et al. which are incorporated by reference herein. The preferred polyester 35 resin mixture is not foamed, although foaming agents may be utilized to decrease the weight of the molded composite article. Additionally, other polyester blends may be used with additional fillers, foaming agents and other

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1 catalysts without departing from the scope of the present
invention, as long as these resin and catalyst
formulations have a sufficiently long cure time to allow
low pressure molding of the molded article of present
5 invention. The use of isocyanate in the resin system is
undesirable since such compounds speed up the curing
process to such an extent that high pressure and high
speed molding processes would be needed, such as RIM or
RRIM, requiring use of the expensive RRIM or RIM high
10 pressure molding apparatus.

Other suitable thermosetting polymeric materials
can include epoxy, acrylic and vinyl esters and blends
thereof which do not contain isocyanate. Additional useful
15 resin compositions suitable for the present invention are
also described in the aforementioned U.S. Patent Nos.
4,844,944 and 4,844,955 to Graefe et al.

In preparing the preferred polyester resin of the
20 present invention, the rigid unsaturated polyester and
flexible unsaturated polyester resins are mixed in mixer
26 and the styrene monomer is then added. DMPT is also
added and thoroughly mixed, and the filler material, such
as calcium carbonate is then mixed typically for about 45
25 to 1 & 1/2 hours. One hundred (100) pounds of the
material is then dispensed into the lined pressure pot 29.
Approximately 3/4 pounds of benzoyl peroxide (CADOX 40E)
cross-linking promoter is added and mixed for about one
30 minute. The pressure pot 29 is closed and pressurized by
compressed air source 30 to about 5 psi. Throttle valve
32 is opened and the air pressure to the pressure pot 29
is increased to about 10 psi. The air pressure is
continuously increased by approximately 5 psi at one
35 minute intervals up to a pressure of from about 20 to
about 25 psi, the pressure is maintained for about 5 to 8
minutes until the mold is filled. After the mold is
filled and some resin mixture spills, the throttle valve
is closed and the clamps are tightened to seal the mold.

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- 1 The molded article is then cured. Curing time after the mold is filled for the above-described mixture is approximately for about 2 minutes to about 22 minutes, preferably from about 2 minutes to about 6 minutes, but it
- 5 may be maintained in the mold for longer times. If the silane based primer is not utilized, curing may range from about forty-five (45) minutes to about 8 or more hours when cured overnight. The longer cure times allow a stronger bond to be formed between the polyester resin and
- 10 the non-finish side 21 of the acrylic shell. After curing has been completed, the mold 36 is opened and the shell support mold closing means is removed. Any overflow of hardened polyester resin adhering to the outside of the molding receptacle 38 is cut away and the molded bathtub
- 15 10 is removed by hand from the molding receptacle 38.

The freshly demolded bathtub 10 is trimmed of excess polyester hardened backing material 14 using suitable equipment. Suitable trimming equipment may

- 20 include the trimming table 60 and horizontally mounted circular saw 62 shown in Figure 6. The finished polyester backed composite bathtub 10 of the present invention is shown in Figure 7A through 7C. Blind Bolts 22 and feet 24, illustrated in Figures 1 and 6 are inserted on the
- 25 bottom surface of the bathtub through the molded polyester backing 14 and into deck supporting board 18.

In a preferred embodiment of the present invention the acrylic shell 12 has a thickness of about 3.2 millimeters while the fiber reinforcement is typically from about 1.0 to 2.0 millimeters measured from the non-finish side 21 of the shell. Typically the total thickness of the molded bathtub is about 8 to 10 millimeters in the side wall region and 20-25 millimeters on the floor region. The total thickness of the deck region may range from about 5 millimeters to about 35 millimeters, preferably from about 8 millimeters to about 30 millimeters. The thickness of the polyester molded

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1 material in the walls is typically from about 4.4 to about
7 millimeters. The preferred tub floor support weight
bearing reinforcing structure is typically made from chip-
board, particle-board, plywood or wooden plank having a
5 preferred thickness of about 7/16 inches, but may range
from about 1/4 inch to about 1/2 half of an inch in
thickness, depending on the desired thickness of the floor
of the molded article and its underlying backing. The
preferred deck supports are typically 1 inch x 1 inch
10 wooden boards as illustrated in Figure 1.

Thus, while we have described what are the
presently contemplated preferred embodiments of the
present invention, further changes and modifications may
15 be made by those skilled in the art without departing from
the scope of the invention, and it is contemplated to
claim all such changes and modifications.

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WE CLAIM:

1. A polymeric composite structure, comprising:
a polymeric shell layer having a finish-side
and a non-finish side;

5 a fiber reinforced resin layer adhered to the
non-finished side of the polymeric shell layer, and a
weight bearing reinforcing structure adhered to said non-
finish side of the polymeric shell layer and to said fiber
reinforced resin layer; and

10 a molded, cross-linked thermosetting polymeric
backing layer, surrounding said fiber reinforced resin
layer and said weight bearing reinforcing structure, which
is bonded to said non-finish side of the polymeric shell
layer, said thermosetting polymeric backing layer includes
15 at least one component selected from the groups comprising
polyester, epoxy, acrylic, vinyl esters and blends
thereof, but does not contain isocyanate.

2. The polymeric composite structure as recited
in claim 1, wherein said non-finish side of said polymeric
shell layer is bonded to said fiber reinforced layer and
molded cross-linked thermosetting backing layer by a
5 silane based coupler.

3. The polymeric composite structure as recited
in claim 2, wherein said silane based coupler comprises a
silane based primer composition and a methylmethacrylate
and solvent blend.

4. The polymeric composite structure recited in
claim 3, wherein said methylmethacrylate and solvent blend
comprises methylene chloride, styrene and water; and

5 wherein said silane based primer composition
further comprises 3[2 vinyl benzylamino)ethylamino]
propyltrimethoxy silane dissolved in toluene, butanol, 2-
butoxy ethanol, and ethyl alcohol.

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5. The polymeric composite structure as recited in claim 1, wherein said polymeric shell layer is an acrylic polymer of polymethylmethacrylate.

6. The polymeric composite structure as recited in claim 1, wherein said fiber reinforced layer comprises a layer of fibers selected from the group consisting of fiberglass, carbon, ceramic, boron, graphite, 5 woolastonite, aromatic polyamide and mixtures thereof; and

10 wherein said weight bearing reinforcing structure is selected from the group consisting of wood, including chip-board, particle-board, plywood, and wooden planks; polymeric composites, and inorganic weight bearing structures.

7. The polymeric composite structure as recited in claim 6, wherein said fiber reinforced layer includes fiberglass; and said weight bearing reinforcing structure includes wooden reinforcing structures positioned below a 5 floor portion and a deck portion of said polymeric shell.

8. The polymeric composite structure as recited in claim 1, wherein said molded, cross-linked thermosetting backing layer, prior to curing comprises a rigid unsaturated polyester resin, a flexible unsaturated 5 polyester resin, a curing promoter, a peroxide cross-linking promoter and a filler in a ratio of from about 2:1 resin to filler, up to about a ratio of 1:30 resin to filler.

9. The polymeric composite structure as recited in claim 8, wherein said filler is selected from the group consisting of calcium carbonate, aluminum trihydrate, glass spheres, sand, ceramic, mica, talc, silica, and 5 mixtures thereof.

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10. The polymeric composite structure as recited in claim 1, having the configuration of a bathtub.

11. A process for manufacturing a polymeric composite structure, comprising:

5 forming a polymeric shell having a finish-side and non-finish side to a suitable shape;

reinforcing the non-finish side of said polymeric shell with a resinous mixture of reinforcing fibers;

10 arranging said reinforced polymeric shell in a mold with said non-finish side covering a weight bearing reinforcing structure placed below weight bearing portions of said polymeric shell;

15 introducing an uncured mixture of unsaturated thermosetting polymeric backing material and cross-linking promoter into said mold at a sufficient pressure to force said backing material to coat the non-finish side of said shell and cover said fiber reinforcing material and said weight bearing reinforcing structure; and

20 curing said molded thermosetting polymeric backing material at a suitable temperature and sufficient time to allow hardening and cross-linking of the thermosetting polymeric material and bonding to said fiber reinforcing material and said non-finish side of the polymeric shell in order to permit demolding of the composite structure without damage.

12. The process for manufacturing a polymeric composite structure as recited in claim 11, further comprising priming said non-finish side of the polymeric shell with a silane based coupler prior to reinforcing.

13. The process for manufacturing a polymeric composite structure as recited in claim 12, wherein said silane based coupler comprises a silane based primer composition and a methylmethacrylate and solvent blend.

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14. The polymeric composite structure recited in claim 13, wherein said methylmethacrylate and solvent blend further comprises methylene chloride, styrene and water; and

5 wherein said silane based primer composition further comprises 3[2(vinyl benzylamino)ethylamino] propyltrimethoxy silane dissolved in toluene, butanol, 2-butoxy ethanol, and ethyl alcohol.

15. The process for manufacturing a polymeric composite structure as recited in claim 11, wherein said reinforcing of the non-finish side includes spray-up and roll down of fibers selected from a group consisting of 5 glass, ceramic, boron, carbon, graphite, woolastonite and aromatic polyamide, in a polyester resin mixture and curing said reinforced fiber resin layer prior to arranging said reinforced shell into the mold.

16. The process for manufacturing a polymeric composite structure as recited in claim 11, wherein said weight bearing reinforcing structure is selected from the group consisting of chip-board, particle-board, plywood, 5 wooden plank, polymeric composites, inorganic weight bearing structures and combinations thereof.

17. The process for manufacturing a polymeric composite structure as recited in claim 11, wherein said thermosetting polymeric backing material includes a mixture of rigid unsaturated polyester resin, flexible 5 unsaturated polyester resin, curing promoter, a peroxide cross-linking promoter and a filler in a ratio from about 2:1 resin to filler up to about 1:30 resin to filler, but does not contain isocyanate.

18. The process for manufacturing a polymeric composite structure as recited in claim 17, wherein said 5 filler is selected from the group consisting of calcium

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carbonate, aluminum trihydrate, glass spheres, ceramic, mica, talc, silica, sand, and mixtures thereof.

19. The process for manufacturing a polymeric composite structure as recited in claim 16, wherein said polymeric composite structure includes a floor and a deck section; and

5 wherein said arranging of the weight bearing reinforcing structure in the mold includes placing said reinforcing structure below said floor and said deck section of the polymeric shell.

20. The process for manufacturing a polymeric composite structure as recited in claim 17, wherein said thermosetting polymeric resin material further includes a foaming agent or reduce the density of said backing material.

5 21. The process for manufacturing a polymeric composite structure as recited in claim 11, wherein said thermosetting polymeric backing material includes at least one component selected from the group comprising polyester, epoxy, acrylic, vinyl esters and blends thereof, but does not contain isocyanate.

22. The process for manufacturing a polymeric composite structure as recited in claim 11, wherein said composite structure has a configuration of a bathtub.

23. A process for manufacturing a polymeric composite structure comprising:

forming a polymeric shell having a finish and non-finish side to a suitable shape;

5 arranging said polymeric shell within a molding cavity with said non-finish side covering a fibrous reinforcing means and weight bearing reinforcing structure suitably arranged in the molding cavity;

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10 introducing an uncured mixture of
thermosetting polymeric backing material and cross-linking
promoter into said mold at a sufficient pressure to force
said polymeric backing material to coat the non-finish
side of said shell and cover said fiber reinforcing
15 material and said weight bearing reinforcing structure;
and

20 curing said molded polymeric backing material
at a suitable temperature and sufficient time to allow
hardening and cross-linking of the polymeric backing
material and bonding to said fiber reinforcing material
and said non-finish side of the polymeric shell to permit
demolding of the composite structure without damage.

5 24. The process for manufacturing a polymeric
composite structure as recited in claim 23, further
comprising priming said polymeric shell a silane based
coupler prior to arranging the shell within the molding
cavity.

25. The process for manufacturing a polymeric
composite structure as recited in claim 24, wherein said
silane based coupler comprises a silane based primer
composition and a methylmethacrylate and solvent blend.

26. The polymeric composite structure recited in
claim 25, wherein said methylmethacrylate and solvent
blend further comprises methylene chloride, styrene and
water; and

5 wherein said silane based primer composition
further comprises 3[2 vinyl benzylamino)ethylamino]
propyltrimethoxy silane dissolved in toluene, butanol, 2-
butoxy ethanol, and ethyl alcohol.

27. The process for manufacturing a polymeric
composite structure as recited in claim 23, wherein said
fibrous reinforcing means includes a mat of fibers which
includes fibers selected from the group consisting of

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5 glass, ceramic, boron, carbon, graphite, woolastonite and aromatic polyamide.

28. The process for manufacturing a polymeric composite structure as recited in claim 27, wherein said fiber reinforcing means is prepared by performing a fiber and resin structure having a shape matching the non-finish 5 side of said shell.

29. The process for manufacturing a polymeric composite structure as recited in claim 23, wherein said weight bearing reinforcing structure is selected from the group consisting of chip-board, particle-board, plywood, 5 wooden plank, polymeric composites, inorganic weight bearing structures and combinations thereof.

30. The process for manufacturing a polymeric composite structure as recited in claim 23, wherein said thermosetting polymeric backing material includes a mixture of rigid unsaturated polyester resin, flexible 5 unsaturated polyester resin, curing promoter, a peroxide-linking promoter and a filler in a ratio from about 2:1 resin to filler up to about 1:30 resin to filler, but does not contain isocyanate.

31. The process for manufacturing a polymeric composite structure as recited in claim 30, wherein said 5 filler is selected from the group consisting of calcium carbonate, aluminum trihydrate, glass spheres, ceramic, mica, talc, silica, sand, and mixtures thereof.

32. The process for manufacturing a polymeric composite structure as recited in claim 23, wherein said polymeric composite structure includes a floor and a deck section; and

5 wherein said arranging of the weight bearing reinforcing structure in the mold includes placing said

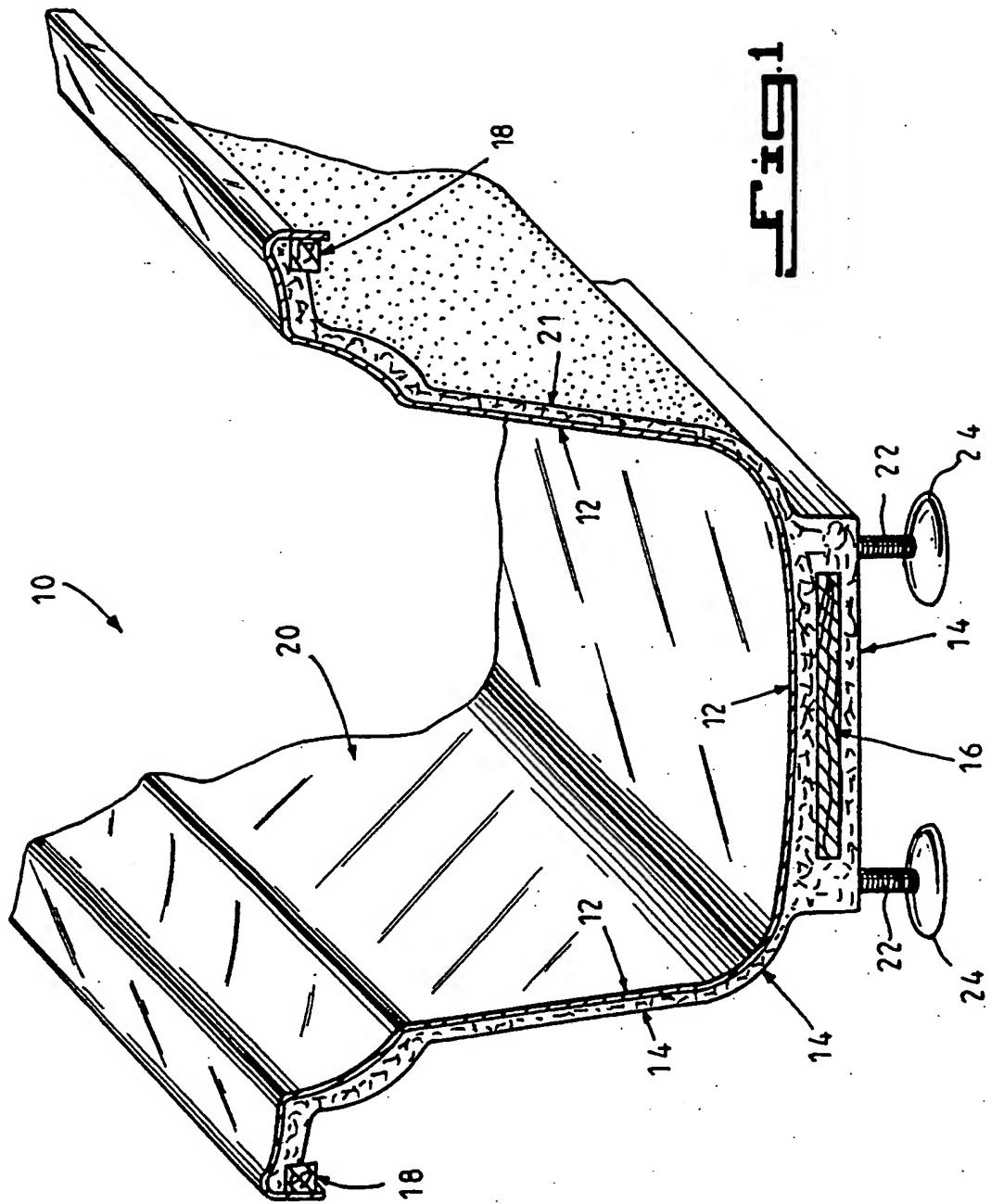
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reinforcing structure below said floor and said deck sections of the polymeric shell.

33. The process for manufacturing a polymeric composite structure as recited in claim 30, wherein said thermosetting polymeric resin material further includes a foaming agent for reduce the density of said backing material.

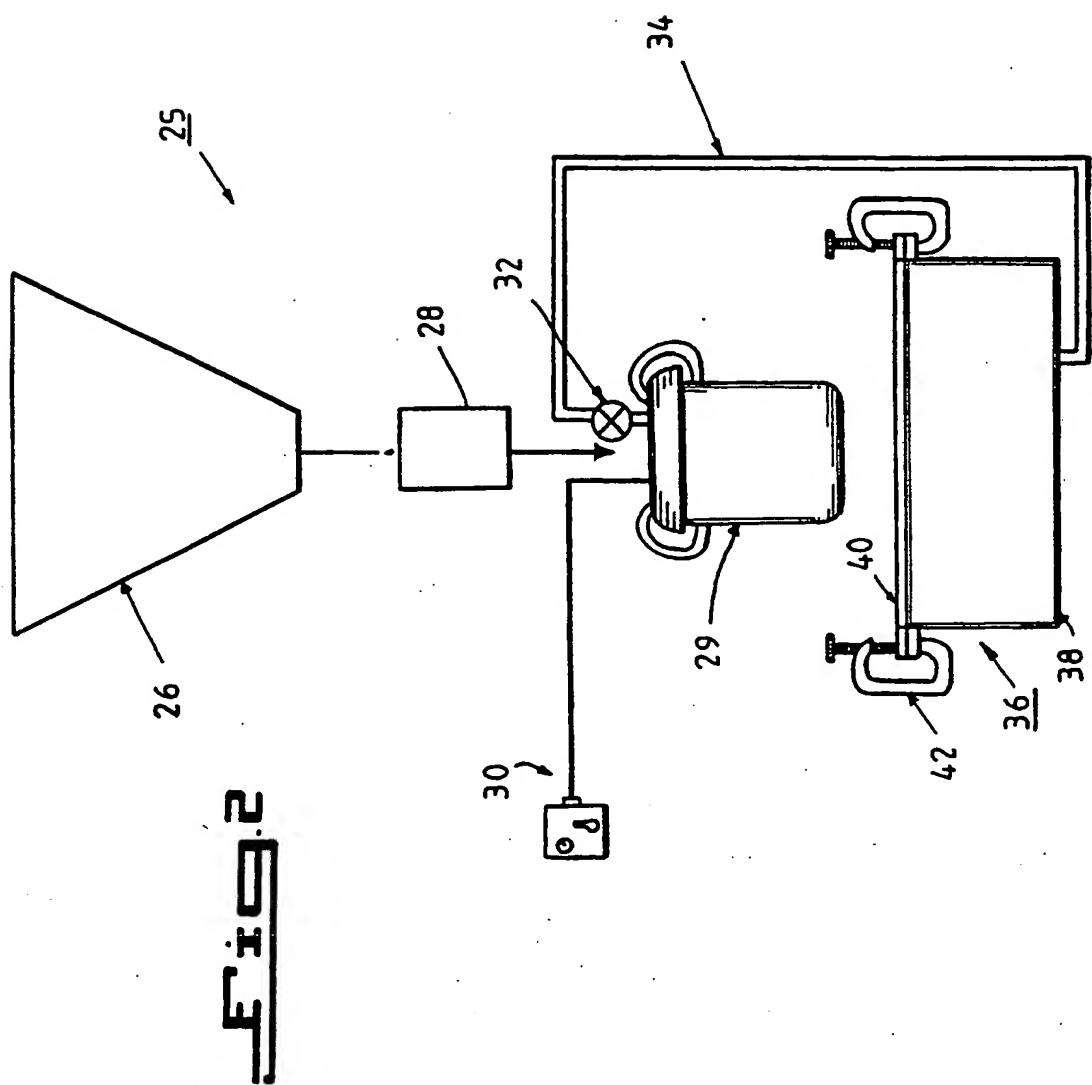
34. The process for manufacturing a polymeric composite structure as recited in claim 23, wherein said thermosetting polymeric backing material includes at least one component selected from the group comprising polyester, epoxy, acrylic, vinyl esters and blends thereof, but does not contain isocyanate.

35. The process for manufacturing a polymeric composite structure as recited in claim 23, wherein said composite structure has a configuration of a bathtub.



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**SUBSTITUTE SHEET**

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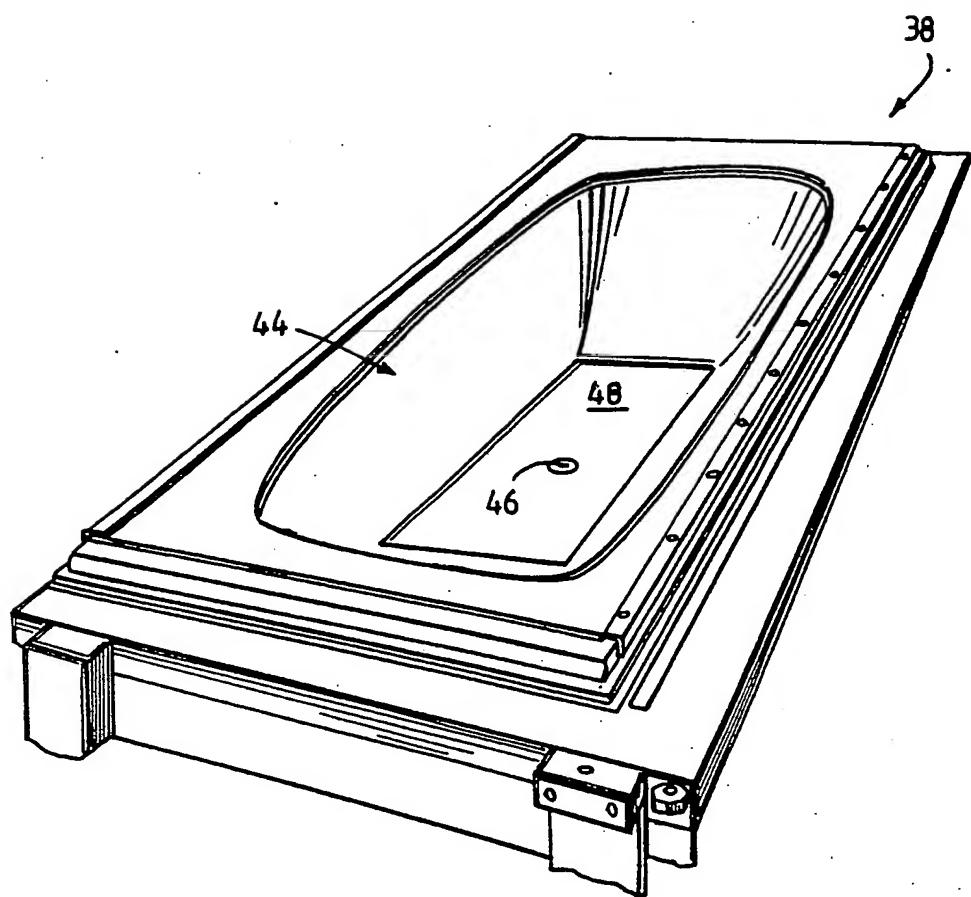
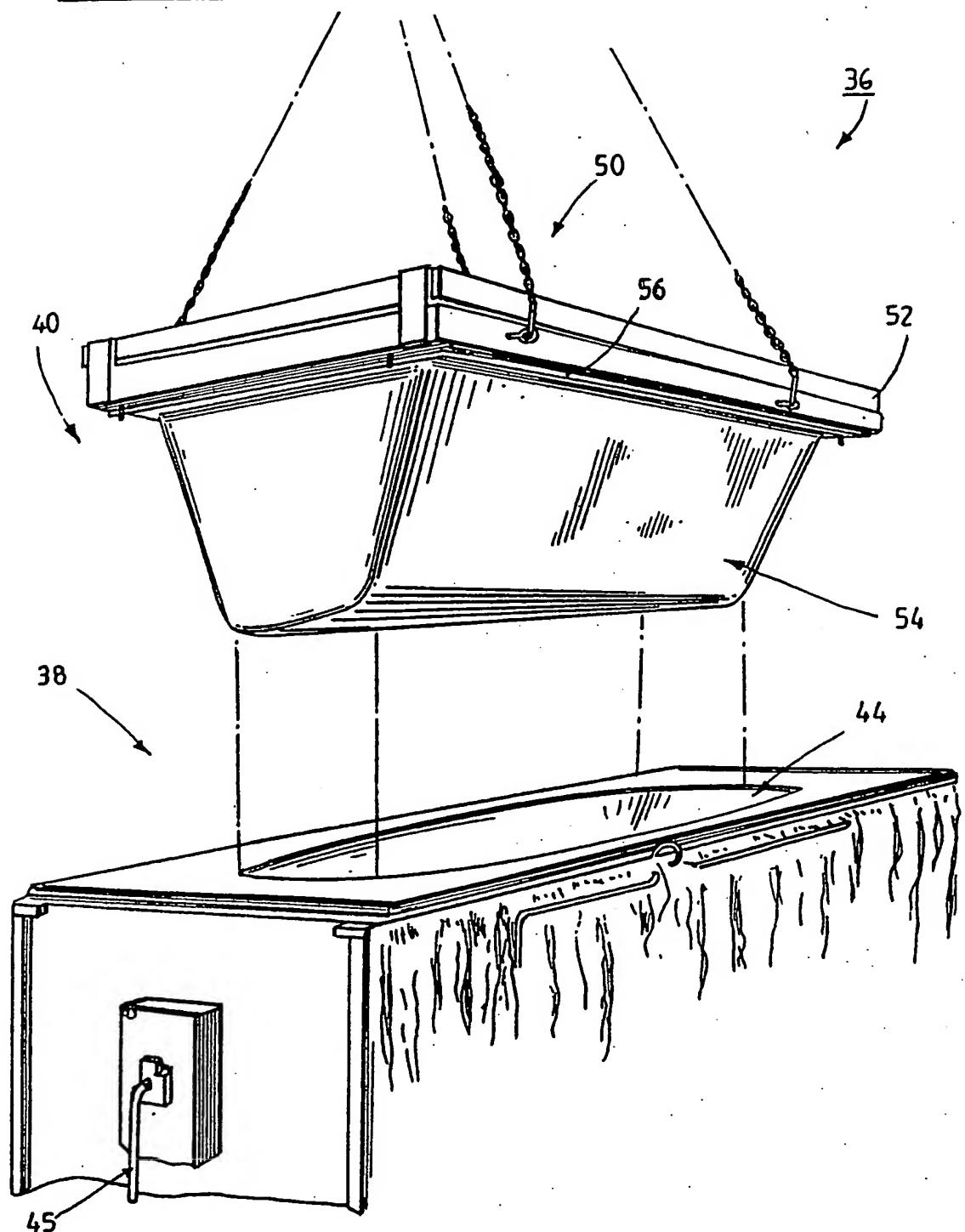


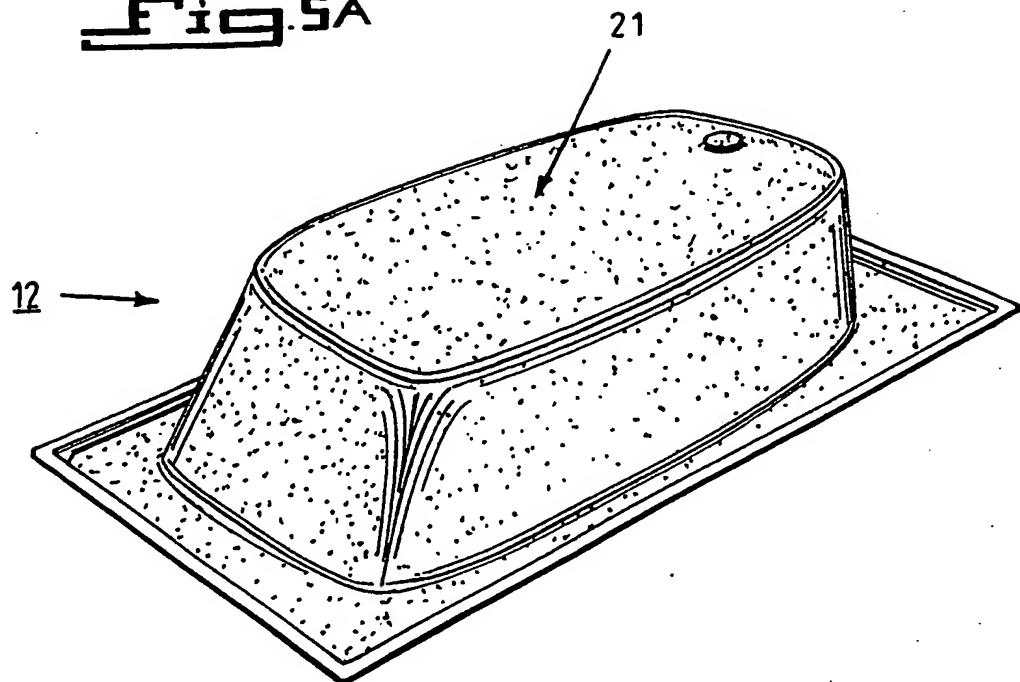
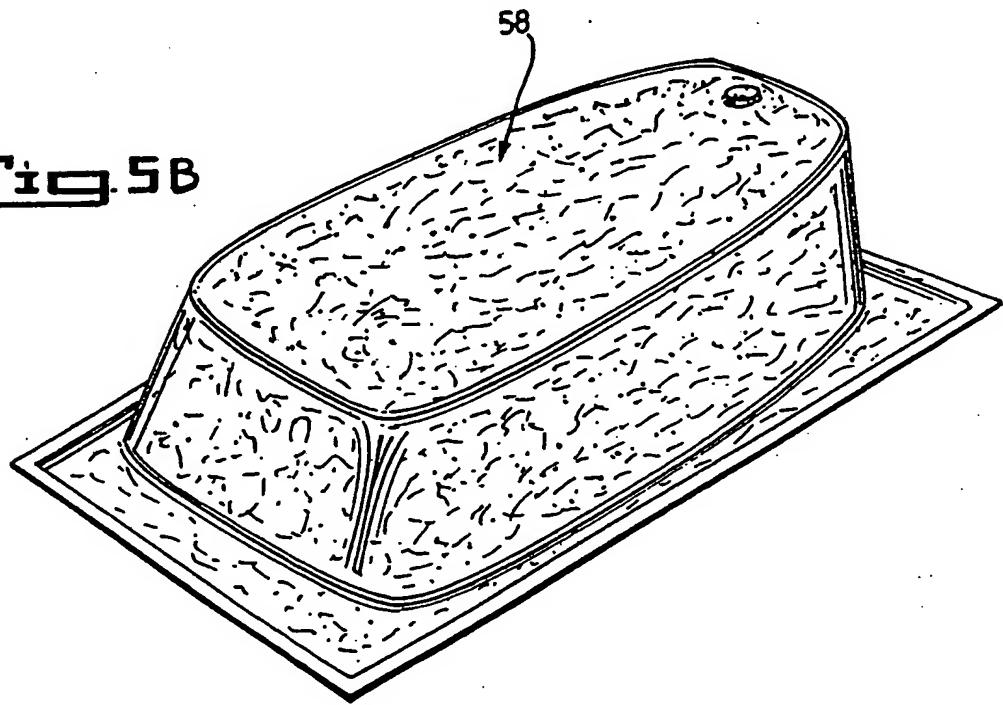
Fig. 3

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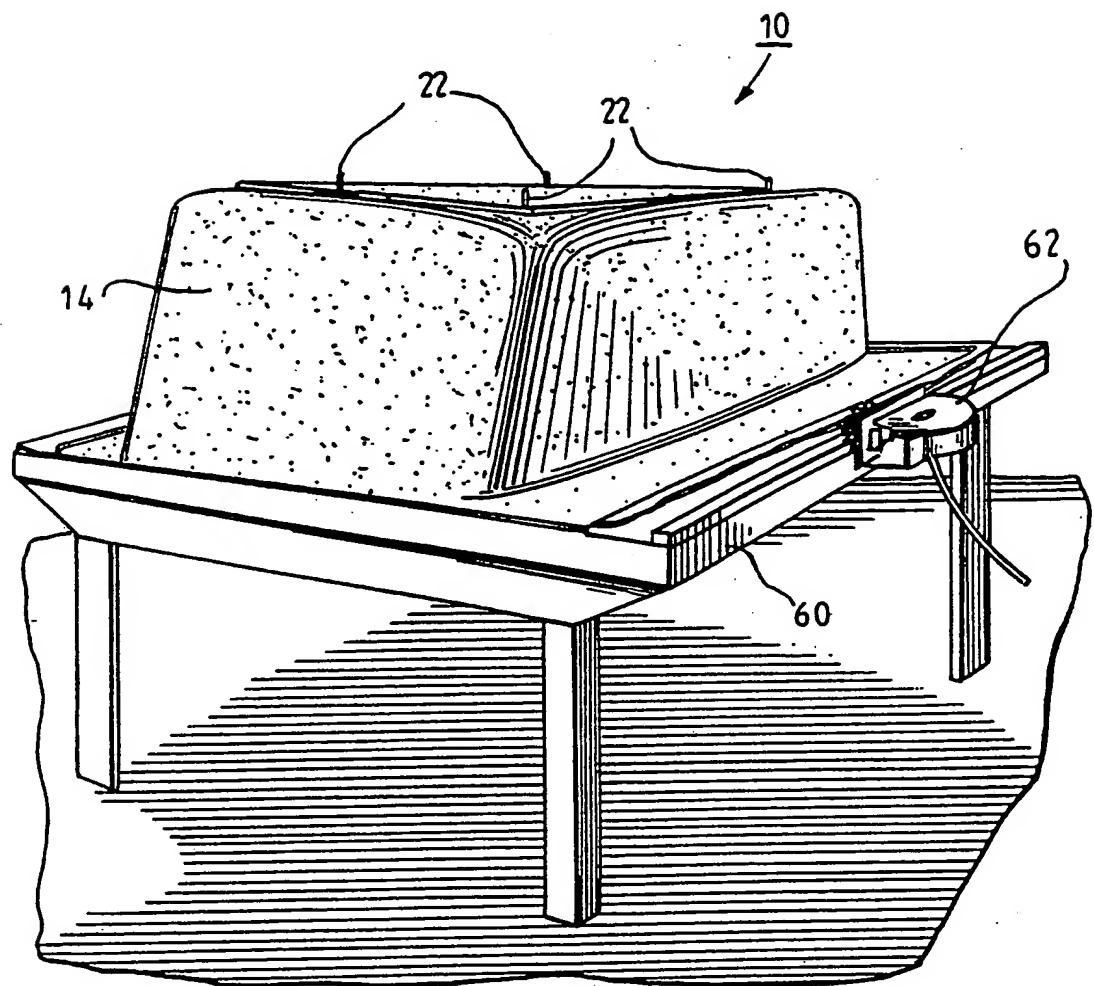
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Fig. 4**SUBSTITUTE SHEET**

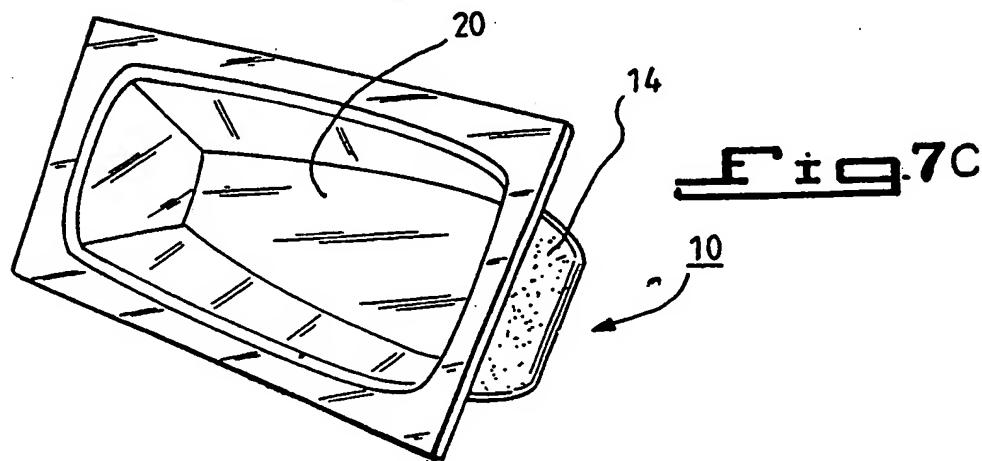
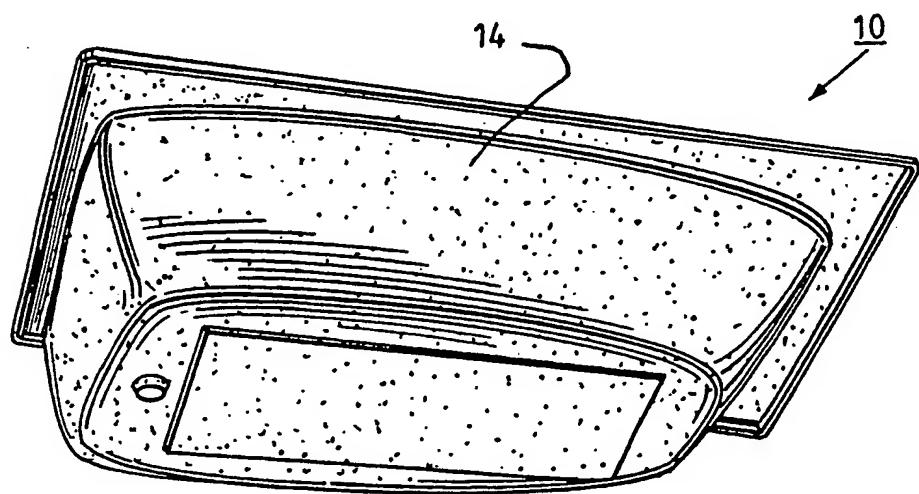
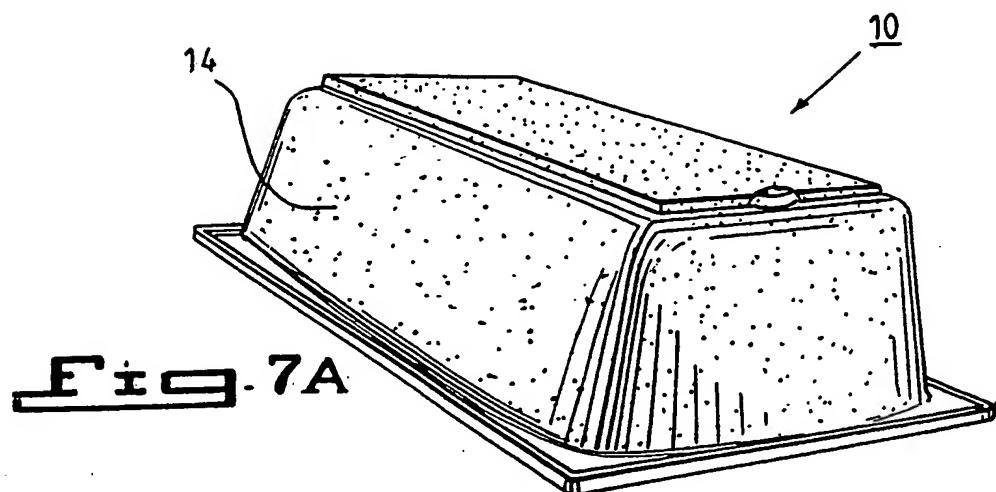
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Fig. 5A**Fig. 5B****SUBSTITUTE SHEET**

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Fig. 6**SUBSTITUTE SHEET**

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 90/02672

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 Int.Cl. 5. B29C67/12 ; A47K3/00 ; B29C67/18

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols		
Int.Cl. 5	B29C	A47K	C08J

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB,A,2087295 (EBDON) 26 May 1982 see the whole document	1, 5-7, 10, 11, 16, 19, 21-23, 27, 29, 32, 34, 35
X	EP,A,2953 (ROHM AND HAAS) 11 July 1979 see page 4, line 3 - page 5, line 35	23, 27, 28, 30, 31, 34, 35
A	see the whole document	1, 5, 6, 15, 17, 18, 21, 22

¹⁰ Special categories of cited documents :

- ^A document defining the general state of the art which is not considered to be of particular relevance
- ^E earlier document but published on or after the international filing date
- ^L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- ^O document referring to an oral disclosure, use, exhibition or other means
- ^P document published prior to the international filing date but later than the priority date claimed

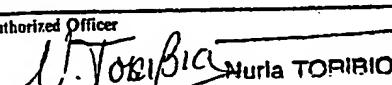
^T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

^X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

^Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

[&] document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 10 JANUARY 1991	Date of Mailing of this International Search Report 12.02.91
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer  Nuria TORIBIO

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,3707434 (STAYNER) 26 December 1972 see the whole document see column 3, lines 33 - 43; claims 4, 5	1, 5-9, 11, 15, 17, 18, 27-30, 31, 34 2-4, 12-14, 24-26
A	US,A,3582388 (STAYNER) 01 June 1971 see column 1, line 66 - column 2, line 27	2-4, 12-14, 24-26
A	GB,A,843863 (FREEDMAN) 10 August 1960 ---	
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A	US,A,4082882 (WEINSTEIN) 04 April 1978 ---	
A	US,A,4664982 (GENOVESE) 12 May 1987 (cited in the application)	
A	US,A,4844944 (GRAEFE) 04 July 1989 (cited in the application)	18, 19

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 90/02672

SA 37147

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A-2087295	26-05-82	None		
EP-A-2953	11-07-79	US-A- 4178406 CA-A- 1114578 JP-A- 54096581 US-A- 4201823		11-12-79 22-12-81 31-07-79 06-05-80
US-A-3707434	26-12-72	None		
US-A-3582388	01-06-71	None		
GB-A-843863		None		
US-A-3720540	13-03-73	None		
US-A-4082882	04-04-78	None		
US-A-4664982	12-05-87	CA-A- 1240248 GB-A,B 2146266 JP-A- 60038147		09-08-88 17-04-85 27-02-85
US-A-4844944	04-07-89	EP-A- 0321264 JP-A- 1259946		21-06-89 17-10-89